

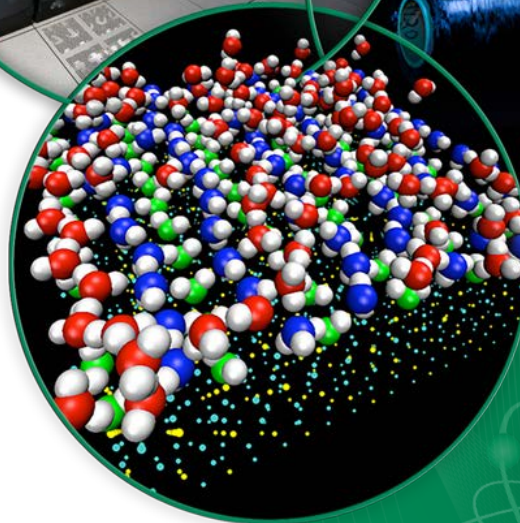
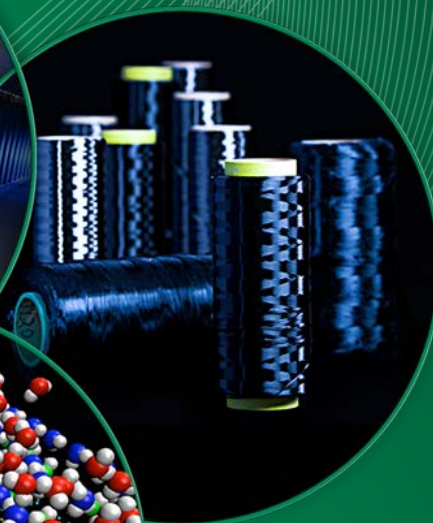
Overcoming Processing Cost Barriers of High-Performance Lithium-Ion Battery Electrodes

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Oak Ridge National Laboratory

June 18, 2014

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Project ID
ES164

Overview

Timeline

- Project Start: 10/1/11
- Project End: 9/30/14
- Percent Complete: 80%

Budget

- Total project funding
 - \$900k
- \$300k in FY12
- \$300k in FY13
- \$300k in FY14

Barriers

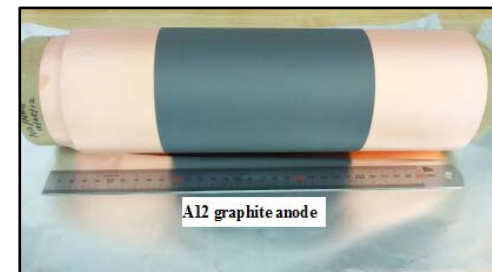
- Barriers Addressed
 - By 2015, reduce PHEV-40 battery cost to \$300/kWh
 - By 2020, further reduce EV battery cost to \$125/kWh.
 - Advanced Li-ion HEV/PHEV battery systems with low-cost electrode architectures.
 - Achieve selling price of \$1700-3400 for 100,000 PHEV units/year by 2015.

Partners






- Interactions/Collaborations
 - National Laboratories: ANL, SNL
 - Battery Manufacturers: XALT Energy, A123 Systems, Navitas Systems
 - Material/Process Suppliers: PPG Industries, Phostech Lithium, TODA America, Superior Graphite, Zenyatta Ventures, Timcal, JSR Micro, Solvay Specialty Polymers, XG Sciences
 - Equipment Manufacturer: Frontier Industrial Technology
- Project Lead: ORNL

Relevance & Objectives

- Main Objective: To transform lithium ion battery electrode manufacturing by the elimination of costly, toxic organic-solvents.
 - Replace NMP processing with water-based chemistry **for all active materials**.
 - Evaluate different commercially available waterborne binders and water-dispersible conductive carbon additives for increased power density.
 - Investigate effect of doubling electrode thicknesses (i.e. develop a thick, high-power cathode architecture).
 - **Elimination of expensive solvent recovery steps, reduction of capital equipment cost, and elimination of expensive inactive components.**
 - FY12 → LiFePO_4 cathode.
 - FY13 → NMC 532 cathode and ConocoPhillips A12 graphite anode.
 - FY14 → NMC 532 and LMR-NMC cathodes and Superior Graphite anode.
- Relevance to Barriers and Targets
 - Implementation of low-cost, green manufacturing methodology for lithium ion battery electrodes using aqueous colloidal chemistry (to meet \$300/kWh 2015 VTO storage goal for PHEV-40s).
 - Correlation of **aqueous** colloidal dispersion properties and **thick** electrode coatings to cell performance to reduce LIB pack cost by **~22% (\$110/kWh-usable reduction)**.
 - **Preserve** long-term performance: achieve a lifetime of 10 years and 1000 cycles at 80% DOD for EVs and 5000 deep discharge cycles for PHEVs.



Project Milestones

Status	Milestone or Go/No-Go	Description
Complete 	FY13 Milestone	Complete round robin testing with ANL and SNL with CP A12 and TODA NMC 532 electrochemical couple.
Complete 	FY13 Milestone	Match full cell performance through 100 cycles of aqueous formulations to NMP/PVDF formulations for CP A12 and TODA NMC 532 electrochemical couple.
Complete 	FY13 Milestone	Match pouch cell (≥ 3 Ah capacity) performance through 100 cycles of aqueous formulations to NMP/PVDF formulations for CP A12 and TODA NMC 532 electrochemical couple.
Complete 	FY14 Milestone	Evaluate three different cathode water-soluble binders (type, molecular weight, etc.) in full coin cells with NMC 532 cathode and CP A12 anode, and down-select for further evaluation (50 0.2C/-0.2C cycles and 50 1C/-2C cycles).
Complete 	FY14 Milestone	Optimize aqueous cathode dispersion with down-selected water-soluble binder and three different conductive carbon additives in full coin cells (50 0.2C/-0.2C cycles and 50 1C/-2C cycles).; down-select conductive carbon additive.
6/2014	FY14 Milestone	Production of large-scale batch (2 L) of cathode NMC 532 aqueous dispersion with down-selected water-soluble binder and conductive carbon black for 1-Ah pouch cell trials.
9/2014	FY14 Milestone	Demonstrate aqueous NMC 532 cathode and graphite anode cycle life through 1000 1C/-2C cycles as compared to NMP/PVDF baseline (in full 1-Ah pouch cells).

Project Approach

- Problems:
 - Excessive agglomeration and settling in aqueous dispersions.
 - Poor wetting and adhesion of water-based dispersions to current collector foils.
 - Solved for LiFePO_4 and NMC 532 on Al foil and CP A12 graphite on Cu foil.
 - Next steps are to qualify Superior Graphite SLC 1520P anode and increase cathode thickness.
- Overall technical approach and strategy:
 1. Chemistry-specific aqueous formulation designs by standardized dispersant selection and rheological optimization methods – Tailored Aqueous Colloids for Lithium-ion Electrodes (TACLE) → **J. Li et al., U.S. Patent Application No. 13/651,270.**
 2. Surface charge measurement, rheology characterization, agglomerate size optimization, order of constituent addition, and mixing protocol optimization.
 3. Coating parameter optimization for TACLE → viscosity control, current-collector surface energy optimization, and tailoring of drying protocol (solved for LiFePO_4 , NMC 532, and CP A12).
 4. Close collaboration with the ANL and SNL ABR efforts, cell manufacturers, active material suppliers, and inactive material suppliers.
 5. ***Scale TACLE methodology with key industry partner such as PPG Industries.***
 6. Systematic study of effects of electrode thickness and calendaring with ANL.
 7. Transition aqueous processing from conventional “power electrode” thicknesses to “energy electrode” thicknesses with high power through optimized cathode architecture (pore-structure gradients for better liquid-phase Li^+ transport).

Project Approach – Pilot-Scale Electrode Processing and Pouch Cell Evaluation: DOE Battery Manufacturing R&D Facility (BMF) at ORNL



Planetary Mixer (≤2 L)



Corona Plasma Treater (Surface Energy Modification)



Slot-Die Coating Line

Dry room for pouch cell assembly

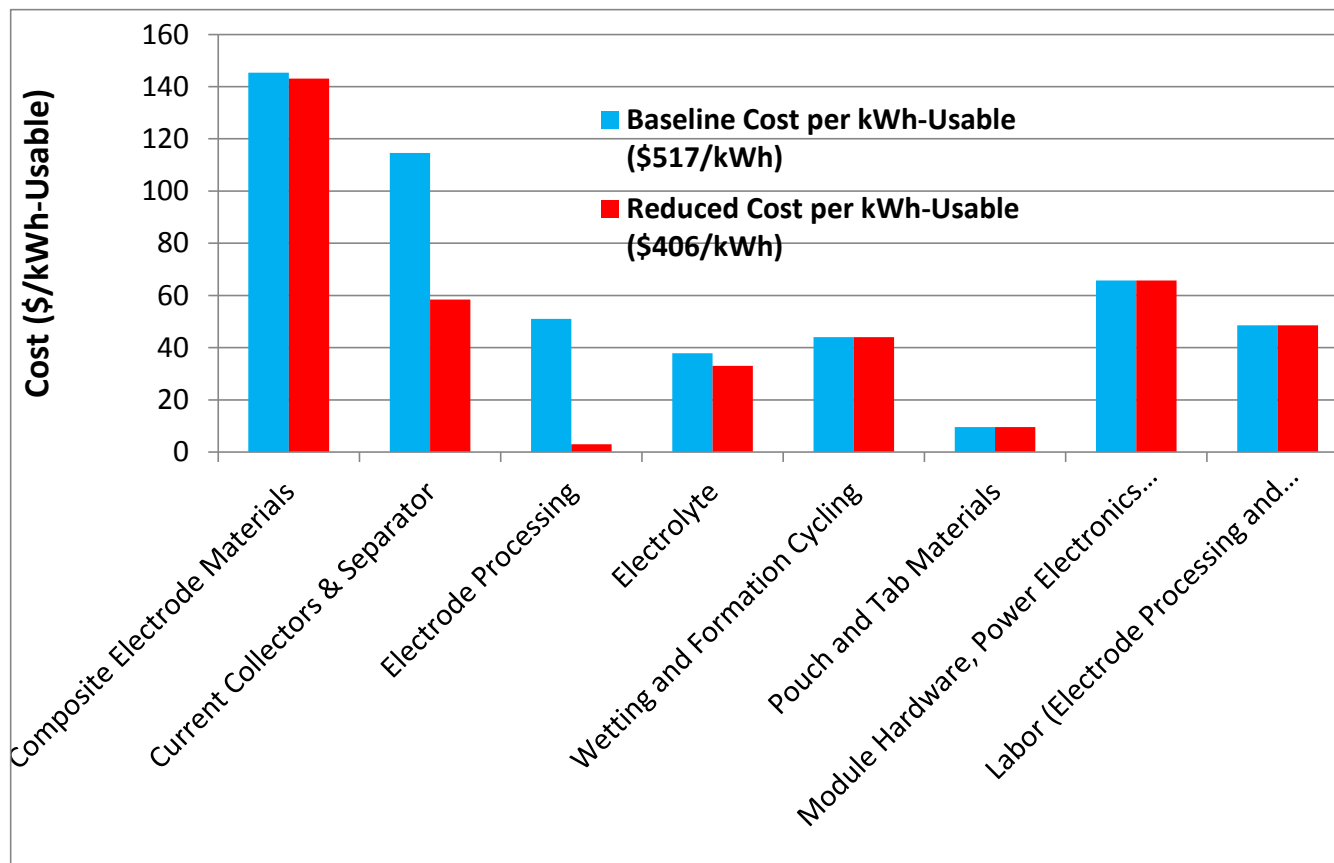
- Largest open-access battery R&D facility in US.
- All assembly steps from pouch forming to electrolyte filling and wetting.
- 1400 ft² (two 700 ft² compartments).
- Humidity <0.5% (-53°C dew point maintained).
- Pouch cell capacity: 50 mAh – 7 Ah.
- Single- and double-sided coating capability.
- Current weekly production rate from powder to pouch cells is 20-25 cells.



Technical Accomplishments – Executive Summary

- FY12 Q1-2: Water-Based LiFePO_4 Half Cells (Presented at 2012 DOE AMR)
- FY12 Q3-4: NMP-Based LiFePO_4 Full Cells (Presented at 2013 DOE AMR)
- FY13 Q1-2: Water-Based LiFePO_4 Full Cells and Water-Based NCM 523 Initial Electrode Qualification (Presented at 2013 DOE AMR)
- **FY13 Q3-4: Water-Based NMC 532 Full Cells, Water-Based CP A12 Full Cells, and Full Pouch Cells (Following Slides)**
- **FY14 Q1-2: Waterborne Binder and Water-Dispersible Conductive Additive Optimization and Full Pouch Cell Scale-Up (Following Slides)**
- FY14 Q3-4: Aqueous NMC 532 Coating Scale-Up and High-Rate Cycle Life; Initial Thick Cathode Trials with Aqueous NMC 532 Formulations
- Specific Accomplishments
 - Obtained **1-3 Ah pouch cell** data for aqueous and NMP processed NMC 532 cathodes through 150 total cycles (50 rate capability cycles + 100 0.2C/-0.2C cycles) with minimal capacity fade.
 - Down-selected Solvay PVDF latex waterborne binder from a thorough screening of different binders for aqueous electrode processing.
 - Initiated systematic electrode thickness study with ANL of the effects on rate capability as a springboard for further development of a thick, high-power cathode from aqueous processing.
- ❖ **All comments from FY13 DOE AMR reviewers have been addressed.**

Technical Accomplishments – Cost Reduction Potential



Physics make water much easier to remove!

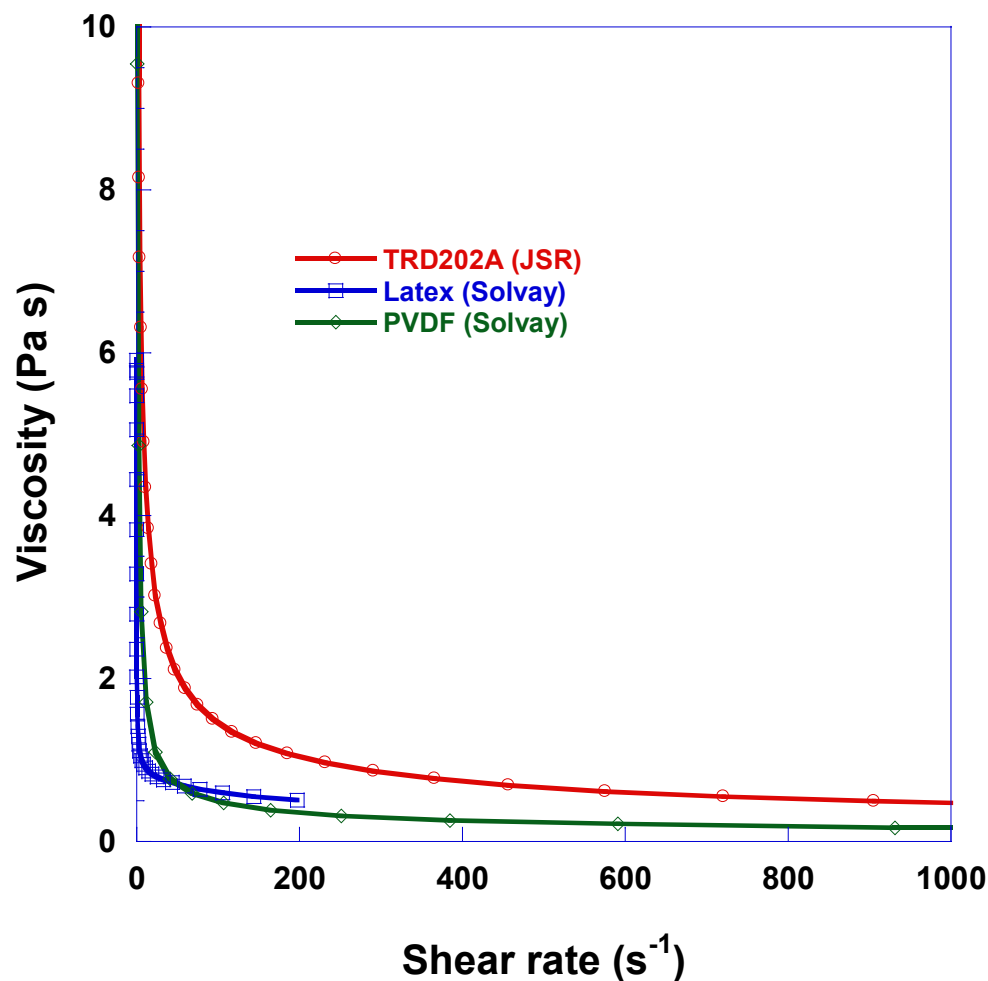
Property	NMP	Water
Heat of Vaporization at 100°C (kJ/mol)	50.6	40.7
Boiling Point (°C)	204.3	100.0
Vapor Pressure at 40°C (mm Hg)	1.0	55.3

- Combination of all-water-based processing plus 2× thicker electrodes has potential of saving \$111/kWh-usable of the **total pack cost** (based on 70% depth of discharge limit).
- Cost of electrode processing could be cut to \$3/kWh-usable primarily due to fast drying of water (i.e. higher solids loading, lower drying T, lower air flow rate & higher volatility than for NMP) and **no solvent recovery costs**.

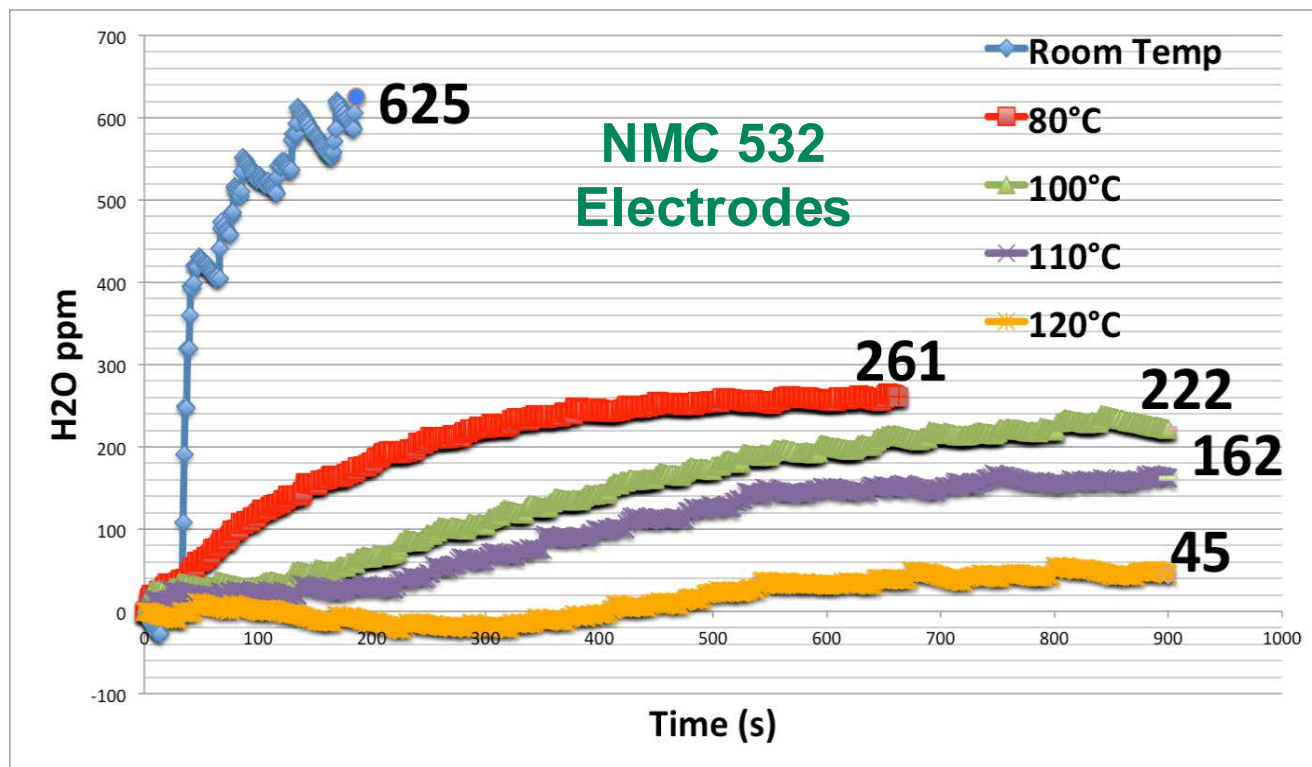
1. D.L. Wood et al., "Prospects for Reducing the Cost of Lithium Ion Electrode Processing and Pouch Cell Formation Steps," J. Power Sources, In Preparation, 2014.
2. D. Howell, "U.S. Battery R&D Progress and Plans," DOE Annual Merit Review, May 14, 2013.
3. K.G. Gallagher et al., "PHEV Battery Cost Assessment," DOE Annual Merit Review, May 9-13, 2011.

Technical Accomplishments – Aqueous Processing Allows for Higher Dispersion Solid Loading (Reduced Solvent Drying)

- Same electrode composition
 - NMC 532/carbon black/binder=90/5/5 wt%
- Binders:
 - 5 wt% PVDF (in NMP)
 - 4 wt% TRD202A & 1wt % CMC (in water)
 - 4 wt% Latex & 1 wt % CMC (in water)
- Solid loading in dispersions:
 - 45 wt% for NMP/PVDF Baseline
 - **60 wt% for TRD202A and Latex (Aqueous)**
- Similar viscosity → higher solid loading can be used in an aqueous system with similar coating “processability”.



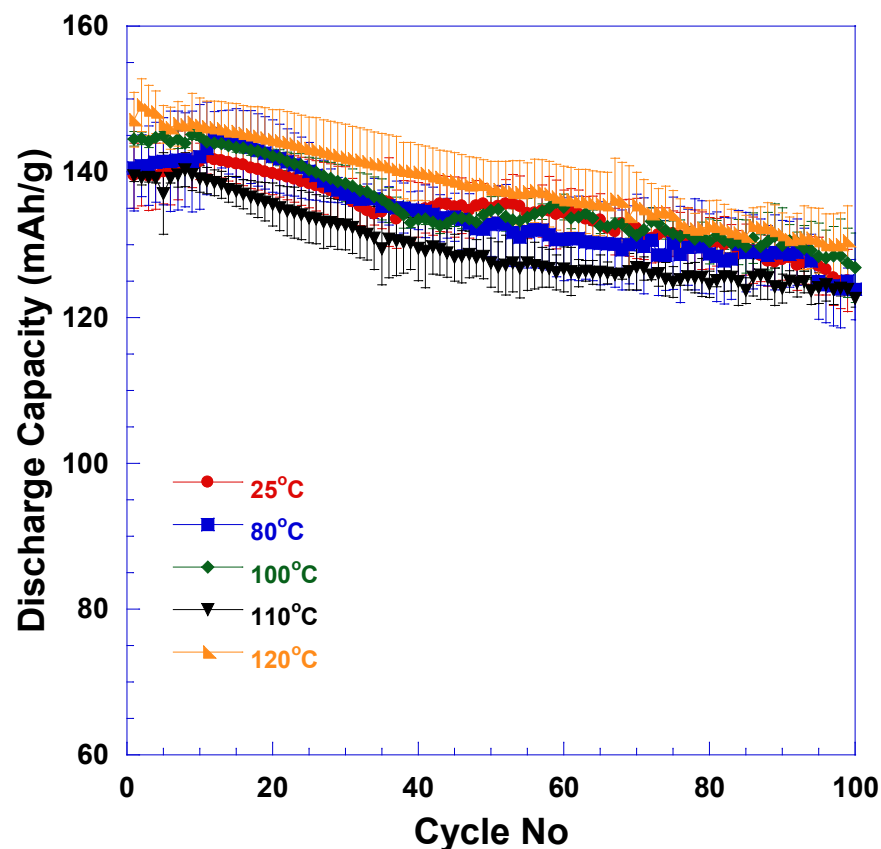
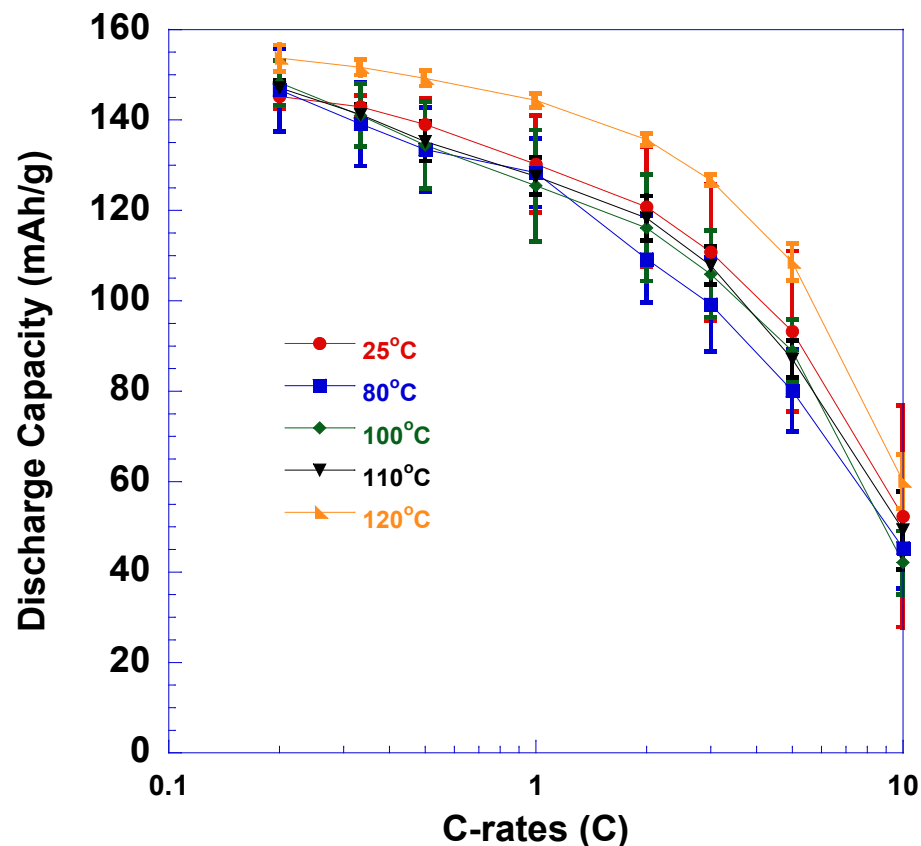
Technical Accomplishments – “Secondary Drying” T Optimized for Aqueous Processing



- Dry-room air with -50 to -55°C dew point used.
- Drying period = 2 hours
- Drying P = 1 atm abs
- Moisture characterized by Karl Fischer titration.

- High T of dry air lowers NMC 532 adsorbed cathode water content to 45 ppm!
- Confirms residual water from all-aqueous processing is not a concern if routine secondary drying conditions are used.
- More effective and energy efficient to use dry-room air to remove trace adsorbed water than vacuum pumping for long time periods.

Technical Accomplishments – Desired Drying Temperature Based on Half Coin-Cell Performance Is 120°C (NMC 532)

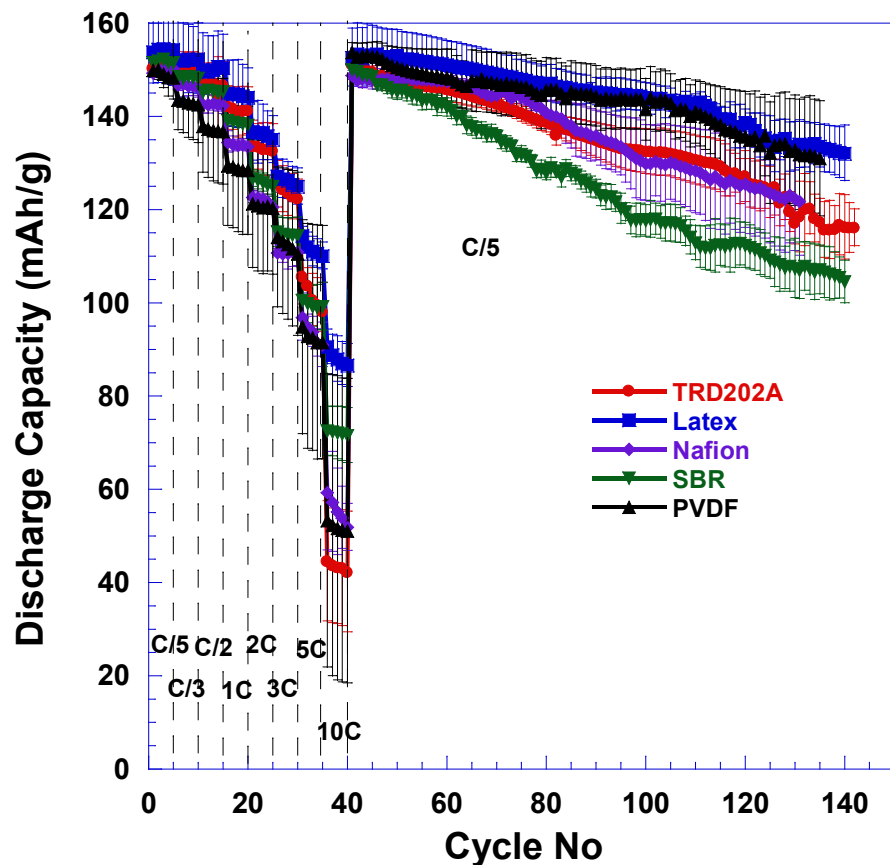


- With JSR Micro TRD202A and as binder and CMC as dispersant.
- Results averaged from three half coin cells
- Rate performance test (left) followed by capacity fade test (right).

Technical Accomplishments – NMC 532

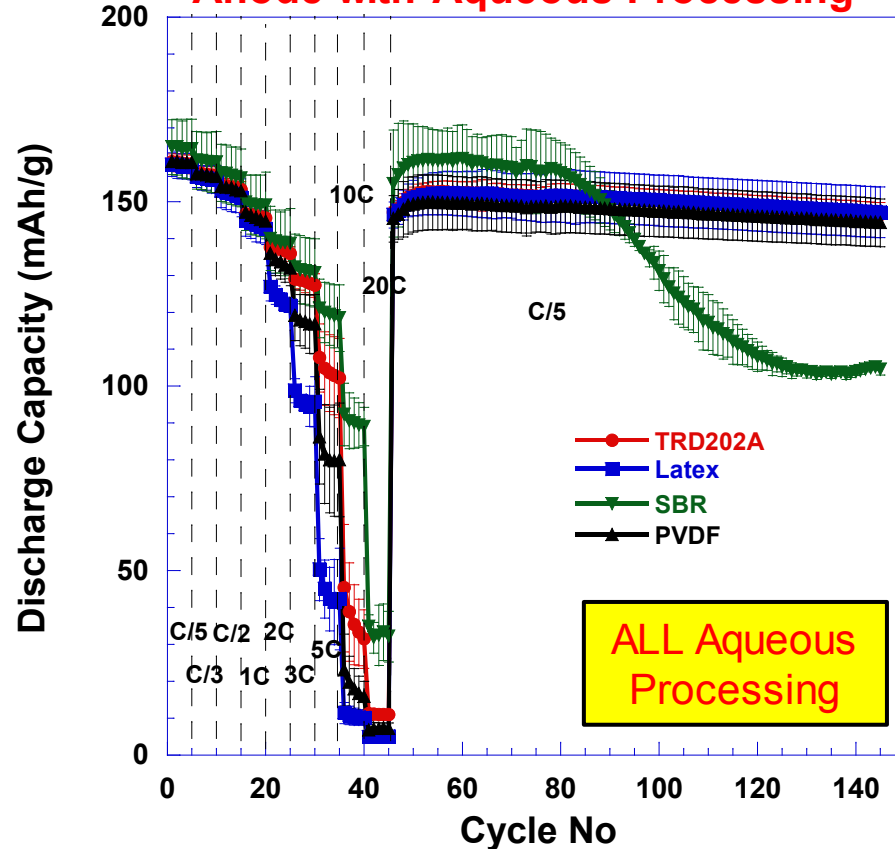
Aqueous vs. NMP/PVDF Processing

Half Coin Cells



2.5 - 4.2 V; 25°C; 1C = 160 mA/g
Capacity normalized to NMC 532 mass.

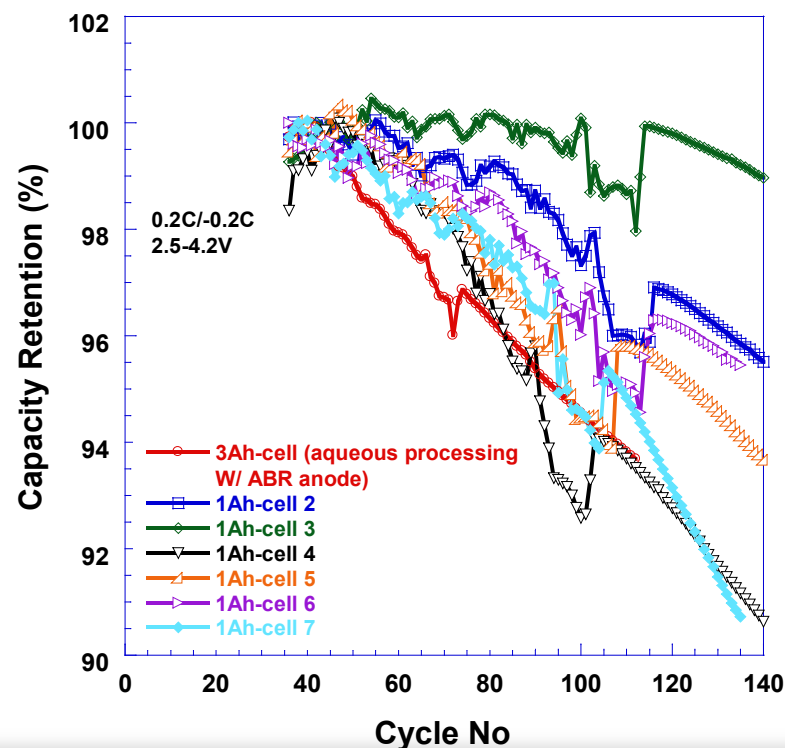
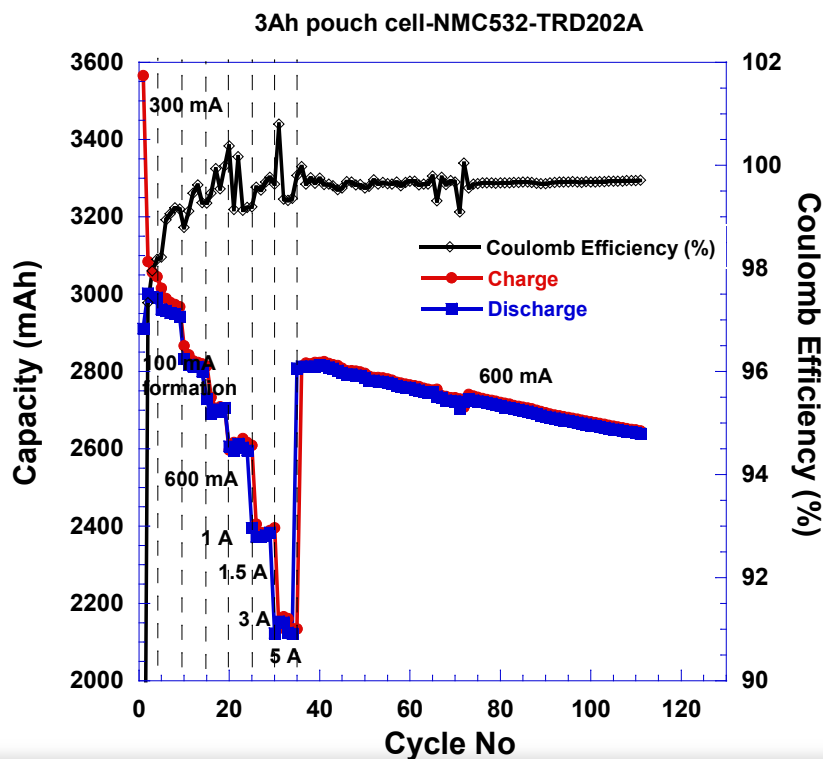
Full Coin Cells: CP A12 Graphite Anode with Aqueous Processing



NMC 532/carbon black/binder/CMC=90/5/4/1 wt%
NMC 532 areal weight: 12.5 mg/cm²
Electrode Balance: N/P=1.1-1.2

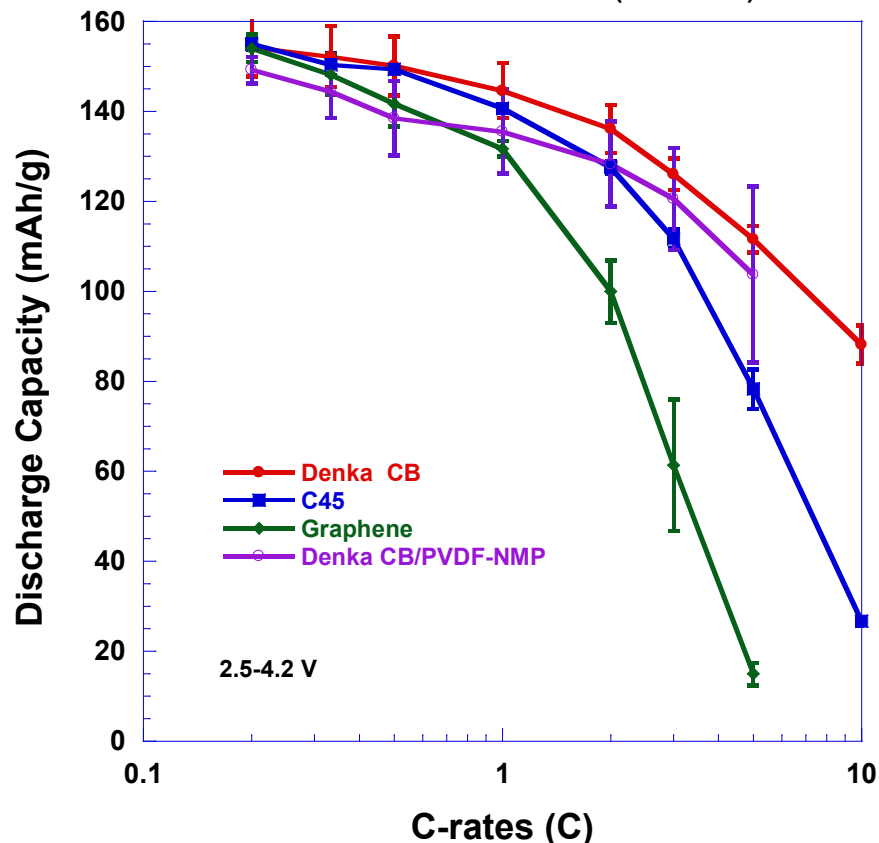
Technical Accomplishments – Down-Selection to Solvay PVDF Latex & 3-Ah Pouch Cell Scaling

- Solvay Specialty Polymers PVDF waterborne latex was selected for further optimization with different conductive carbon additives.
- Basis for down-selection was high half-cell rate capability, excellent full coin cell capacity fade, and likely US production of binder.
- Aqueous formulations (**both** ABR anode and cathode baselines) were scaled to a 3-Ah pouch cell and compared to six 1-Ah pouch cells with baseline NMP/PVDF processing.

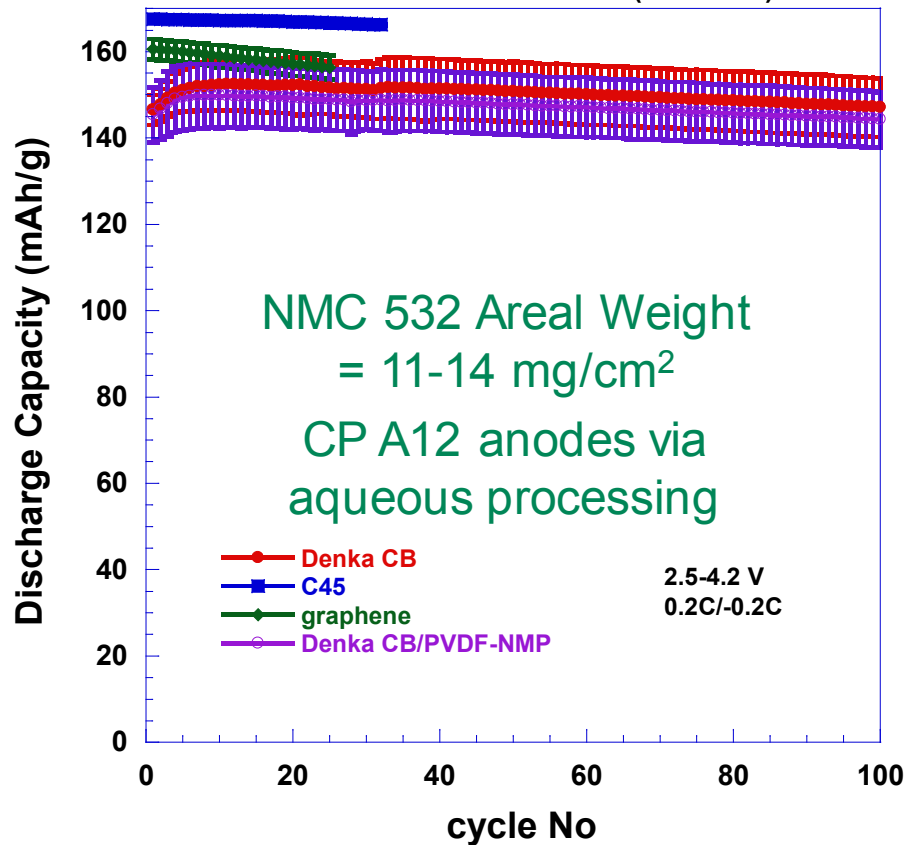


Technical Accomplishments – Conductive Carbon Additive Optimization with Aqueous Processing

Comparison in rate performance NMC532 cathodes with various carbon blacks (Half cells)



Comparison in cyclic performance NMC532 cathodes with various carbon blacks (Full cells)



- NMC 532 with Denka carbon black via aqueous processing matches rate performance of that via NMP-based processing.
- NMC 532 cathodes with various carbon blacks show comparable or superior cycling performance to baseline electrodes.

Selected Responses to Specific FY13 DOE AMR Reviewer Comments – 1

- Third reviewer identified need to address rheology, wetting, film formation application, and drying through the formulation parameters.
 - These topics are routinely addressed as part of the aqueous formulation development and are a standard part of the project approach.
 - The project approach slide shows how these considerations are tackled from dispersion preparation through coating drying and back-up technical slides with examples were added.
- Fourth reviewer identified that anode aqueous processing has been used in Japan for many years and that binder electrochemical stability needs to be checked (especially xanthan gum).
 - This comment is why we focus on cathode aqueous processing development, which is still highly developmental.
 - In addition, the Japanese aqueous anode formulations are proprietary, so work that develops new anode formulations for domestic battery maker use is desirable.
 - Cyclic voltammetry is routinely used to examine binder stability to oxidation in the cathodes.
 - Xanthan gum was a starting point for the project to show that even a polysaccharide binder can be successfully implemented at the cathode; commercial waterborne polymer binders are now the basis for the research.
- Fourth reviewer also expressed an interest in seeing cost reduction potential of aqueous processing.
 - Slide 8 was added with the impact of aqueous processing and thick electrode coatings on LIB pack cost.

Collaborations

• Partners

- National Labs: Argonne National Laboratory, Sandia National Laboratories
- Battery Manufacturers: XALT Energy, A123 Systems, Navitas Systems
- Active Material Suppliers: Phostech Lithium, TODA America, Superior Graphite, Zenyatta Ventures
- Inactive Material Suppliers: JSR Micro, Solvay Specialty Polymers, Timcal, XG Sciences
- Equipment/Coating Suppliers: PPG Industries, Frontier Industrial Technology



• Collaborative Activities

- Electrode formulation, coating standardization, electrode thickness effect, and round robin electrode testing with VTO ABR baseline active materials (with ANL and SNL); ORNL's unique contributions are aqueous dispersions and coatings.
- Selection of appropriate dispersants and water-soluble binders for aqueous processing and thick electrode development (with Solvay Specialty Polymers and JSR Micro).
- Scale-up logistics and manufacturing cost savings of aqueous electrode processing with key coating experts (PPG Industries and Frontier Industrial Technologies).

Future Work

- Remainder of FY14
 - Finish study of effect of conductive carbon additive and waterborne binder interaction on rate performance.
 - Aqueous processing of LMR-NMC cathodes to support high-energy cell commercialization.
 - Assist binder suppliers with commercialization of water-soluble binders.
 - Scale-up trials with a select battery-supplier partner's equipment or a coating company such as PPG industries.
 - Begin thick cathode coating experiments with aqueous NMC 532 cathode formulation; investigate effect of calendaring on pore structure.
 - Supply ANL, SNL, and select industry partner with 100-ft rolls with 8" coating width of water-based anodes and cathodes.

Summary

- **Objective:** this project facilitates lowering the unit energy cost by up to \$110/kWh-usable of EVs and PHEVs by addressing the expensive electrode coating and drying steps.
- **Approach:** blends colloidal and surface science with manufacturing science (coating, drying, etc.) to enable implementation of aqueous processed electrodes.
 - Raw material (solvent and binder) and processing costs are addressed.
 - $\text{LiFePO}_4 \rightarrow \text{NMC 532}$ and $\text{CP A12} \rightarrow \text{Superior Graphite SLC 1520P}$ and TODA HE5050
 - Ease of technology scale-up (capital costs reduced and cell production costs eliminated).
- **Technical:** Demonstrated cycling performance in full coin cells and 3-Ah pouch cell with water-based NMC 532 and CP A12; down-selected optimal waterborne PVDF latex binder and determined optimal secondary drying protocol for aqueous processing.
- All FY14 milestones are on schedule.
- **Collaborators:** Extensive collaborations with national laboratories, lithium-ion battery manufacturers, raw materials suppliers, and coating producer.
- **Commercialization:** Highly engaged with potential licensees; high likelihood of technology transfer because of significant cost reduction benefits and equipment compatibility.

Acknowledgements

- U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (Program Managers: David Howell and Peter Faguy)
- ORNL Contributors:
 - Claus Daniel
 - Jianlin Li
 - Beth Armstrong
 - Brad Brown
 - Debasish Mohanty
 - Shrikant Nagpure
- Technical Collaborators:
 - Andrew Jansen
 - Bryant Polzin
 - Chris Orendorff
 - David Telep
 - Erin O'Driscoll
 - Maneesh Bahadur
 - Mike Wixom
 - James Banas
 - Gregg Lytle
 - Jack Burgman
 - Stuart Hellring



Phostech Lithium



Information Dissemination and Commercialization

- Patent
 - J. Li, B.L. Armstrong, C. Daniel, and D.L. Wood, “Aqueous Processing of Composite Lithium Ion Electrode Material,” Filed October 12th, 2012, U.S. Patent Application No. 13/651,270 (UT-Battelle, LLC).
- Refereed Journal Papers and Book Chapter
 1. J. Li, C. Daniel, and D.L. Wood, “Cathode Manufacturing for Lithium-Ion Batteries,” in *Handbook of Battery Materials*, C. Daniel and J.O. Besenhard, Editors, 2nd Edition, pp. 939-960, Wiley-VCH, Weinheim, Germany (2011).
 2. J. Li, C. Daniel, and D.L. Wood, “Materials Processing for Lithium-Ion Batteries,” *Journal of Power Sources*, **196**, 2452–2460 (2011).
 3. J. Li, C. Rulison, J. Kiggans, C. Daniel, and D.L. Wood, “Superior Performance of LiFePO₄ Aqueous Dispersions via Corona Treatment and Surface Energy Optimization,” *Journal of The Electrochemical Society*, **159**, A1152–A1157 (2012).
 4. J. Li, B.L. Armstrong, J. Kiggans, C. Daniel, and D.L. Wood, “Optimization of LiFePO₄ Nanoparticle Suspensions with Polyethyleneimine for Aqueous Processing,” *Langmuir*, **28**, 3783–3790 (2012).
 5. J. Li, B.L. Armstrong, J. Kiggans, C. Daniel, and D.L. Wood, “Lithium Ion Cell Performance Enhancement Using Aqueous LiFePO₄ Cathode Dispersions and Polyethyleneimine Dispersant,” *Journal of The Electrochemical Society*, **160**, A201–A206 (2013).
 6. J. Li, B.L. Armstrong, J. Kiggans, C. Daniel, and D.L. Wood, “Optimization of Multicomponent Aqueous Suspensions of LiFePO₄ Nanoparticles and Carbon Black for Lithium Ion Battery Cathodes,” *Journal of Colloid and Interface Science*, **405**, 118–124 (2013).
 7. D.L. Wood, C. Daniel, and J. Li, “Prospects for Reducing the Cost of Lithium Ion Electrode Processing and Pouch Cell Formation Steps,” *Journal of Power Sources*, In Preparation, 2014.
- Selected Presentations (4 out of 11)
 1. D. Wood, J. Li, D. Mohanty, S. Kalnaus, B. Armstrong, C. Daniel, and B. Brown, “Advanced Materials Processing and Novel Characterization Methods for Low-Cost, High Energy-Density Lithium-Ion Batteries,” Advanced Automotive Battery Conference 2013, Pasadena, California, February 4-8, 2013. **(Invited)**.
 2. C. Daniel, D. Wood, J. Li, B. Armstrong, J. Kiggans, D. Mohanty, and S. Kalnaus, “Electrification of Transportation – Cost and Opportunities”, Bridging the Gap Conference 2013, Oak Ridge, Tennessee, March 5-6, 2013 **(Invited)**.
 3. J. Li, D. Mohanty, B. Brown, C. Daniel, and D. Wood, “Fabrication and Performance of LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ Cathodes through Aqueous Processing with Various Binders,” Advanced Automotive Battery Conference 2014, Atlanta, Georgia, February 4, 2014. **(Invited)**.
 4. J. Li, D. Mohanty, C. Daniel, and D. Wood, “Aqueous Processing of LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ Composite Cathodes for Lithium-Ion Batteries,” 225th Meeting of The Electrochemical Society, Orlando, Florida, Abstract No. 194, May 11-16, 2014.

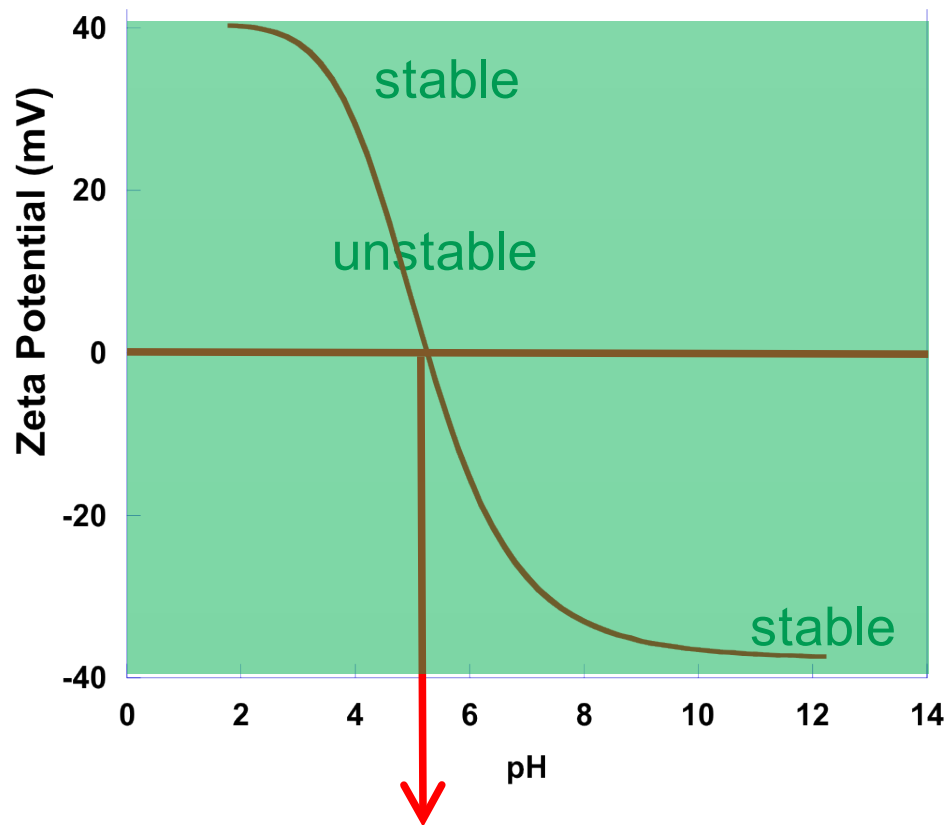
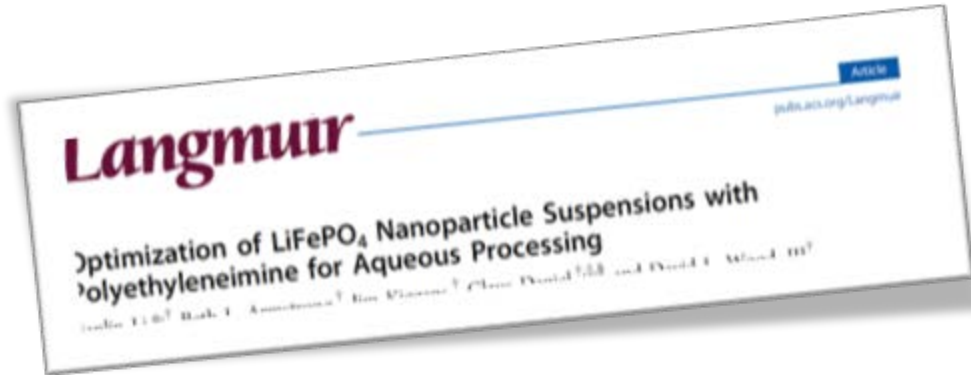
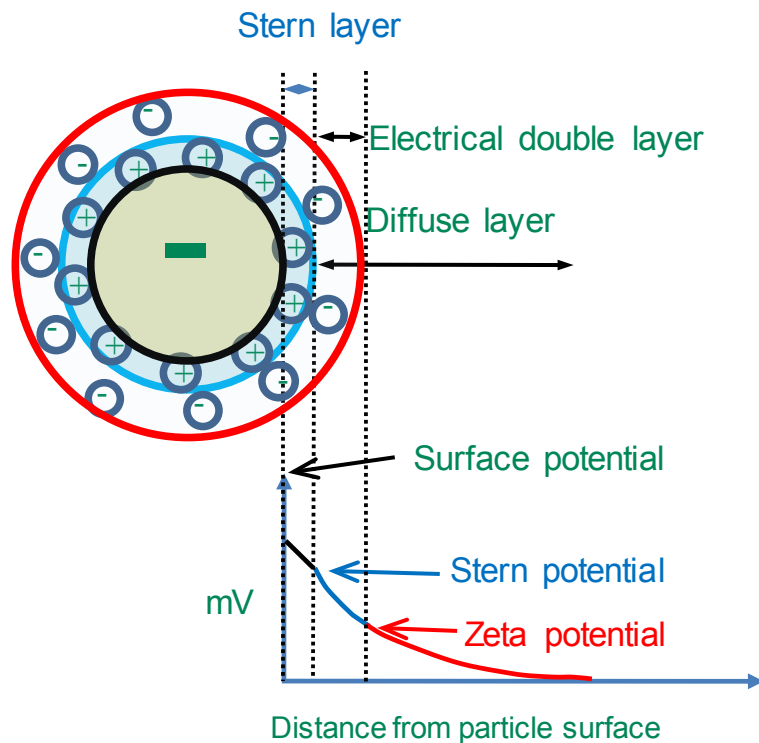


Fisker Karma

Thank you for your attention!

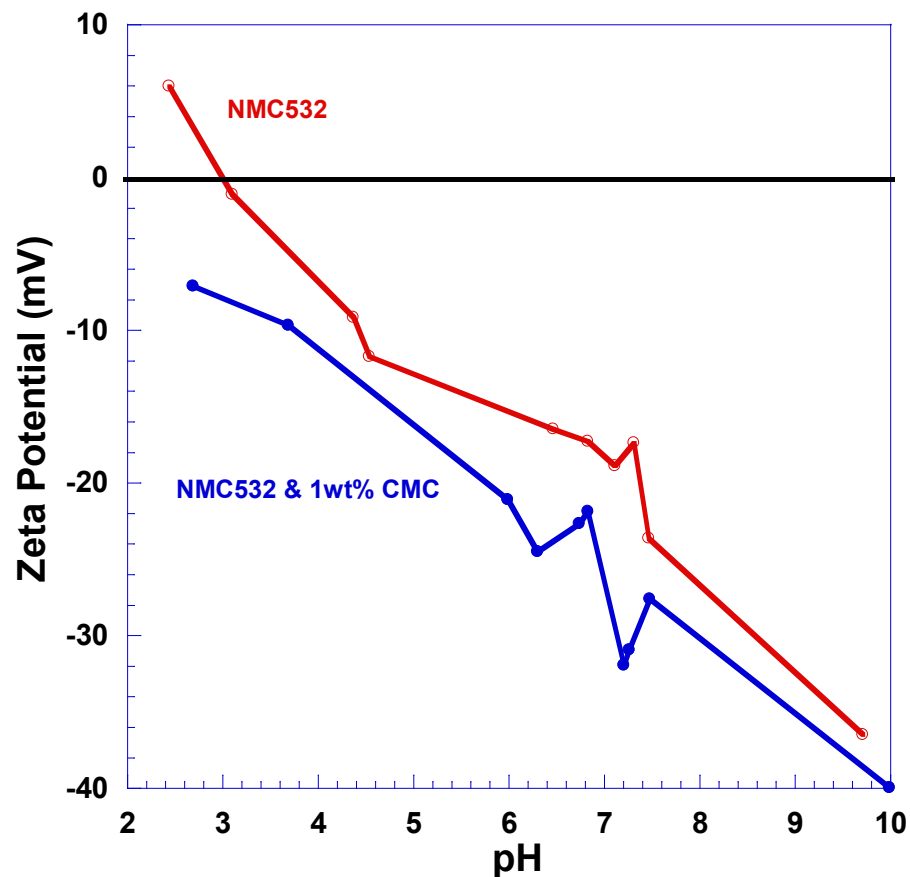
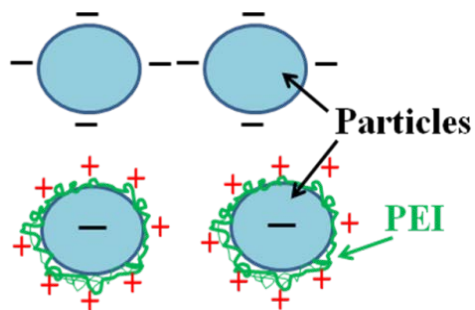
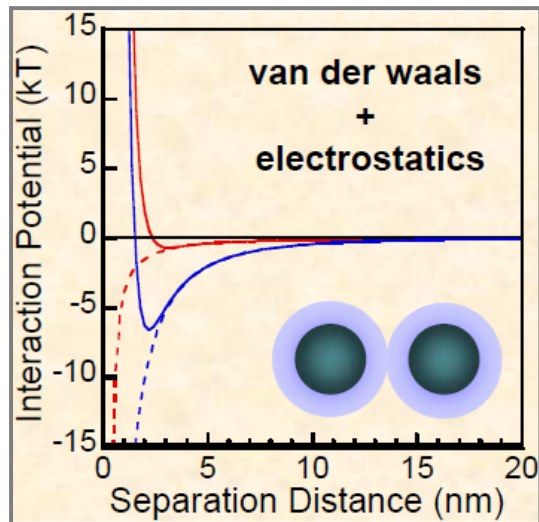
Technical Back-Up Slides

Zeta potential is used to characterize surface charge



Isoelectric point (IEP): least stable

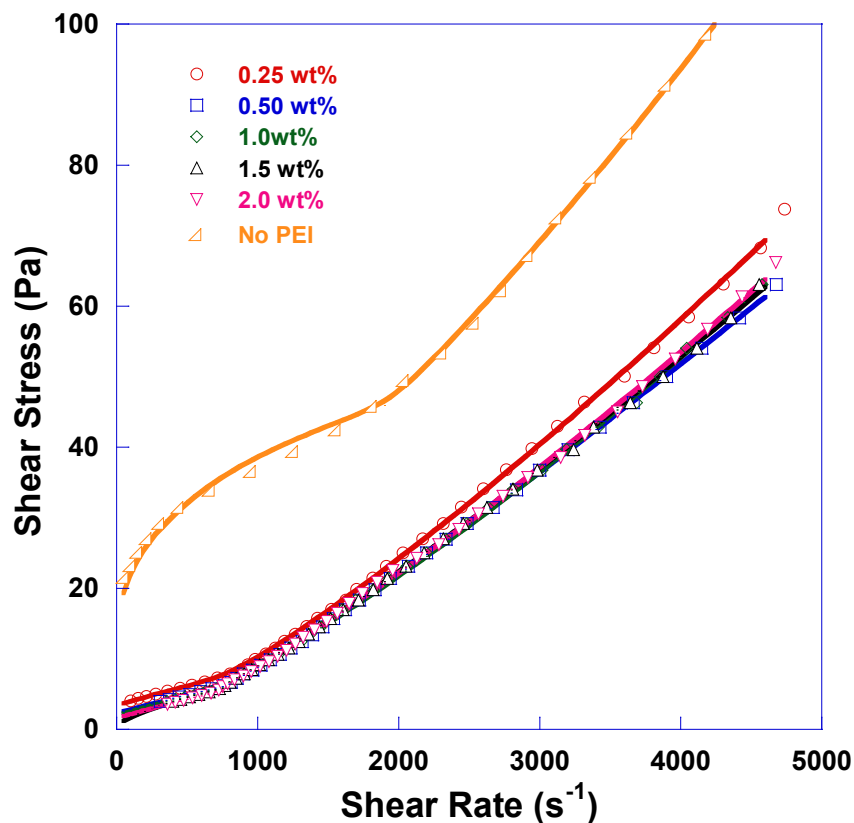
CMC Improves Stability of Water-Based NMC 532 Suspension



- Carboxymethyl cellulose: MW = 250,000 g/mol, DS=0.7

Newtonian Behavior with PEI > 0.25 wt%

LiFePO₄ / PEI / H₂O = 100 / 0-2 / 350 wt fraction, MW=600 g/mol



Herschel-Bulkley (H-B) model

$$\begin{cases} \tau = \tau_0 + K \dot{\gamma}^n & \text{if } \tau > \tau_0 \\ \dot{\gamma} = 0 & \text{if } \tau \leq \tau_0 \end{cases}$$

where τ , τ_0 , K , $\dot{\gamma}$ and n are the shear stress, yield stress (stress needed to initiate the flow), consistency index, shear rate and power-law index, respectively

$$\begin{cases} n < 1 & \text{shear thinning} \\ n = 1 & \text{Newtonian} \\ n > 1 & \text{shear thickening} \end{cases}$$

Power-Law Index

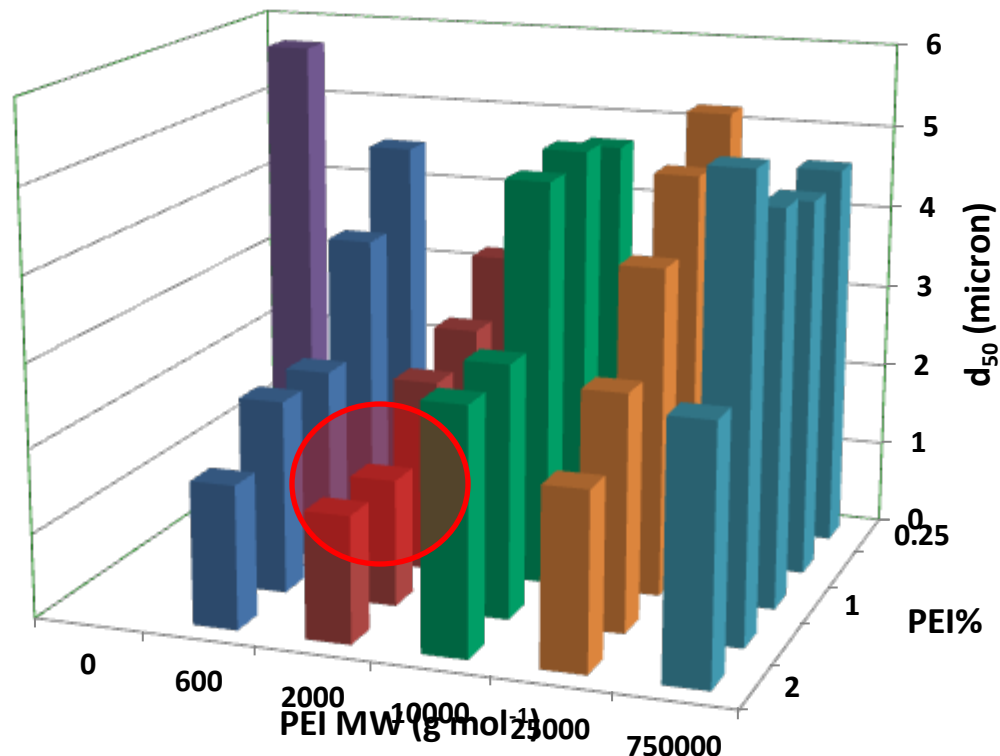
J. Li et al., *Journal of Colloid and Interface Science*, 405, 118–124 (2013).

	0%	0.25%	0.50%	1.00%	1.50%	2.00%
Low $\dot{\gamma}$	0.32	0.87	0.92	0.94	0.96	0.99
high $\dot{\gamma}$	1.37	1.27	1.18	1.28	1.21	1.25

Optimal PEI Conditions: 1.5 wt% PEI (MW=2,000 g/mol)

LiFePO₄ dispersion

PEI is based on LiFePO₄ weight fraction



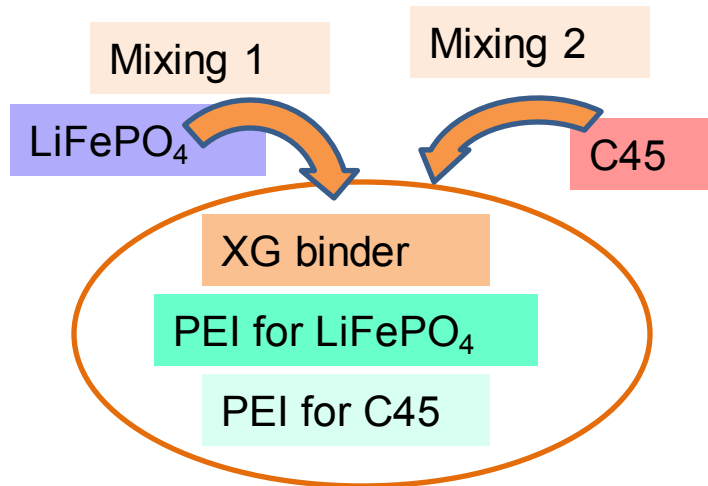
J. Li *et al.*, *Journal of Colloid and Interface Science*, 405, 118–124 (2013).

- The addition of PEI dramatically reduces agglomerate size
- Agglomerate size decreases with increasing PEI%
- Agglomerate size decreases with increasing PEI MW from 600 to 2000 g/mol and mostly increases with further increasing PEI MW
- Minimum agglomerate size obtained at 1.5 wt% and 2.0 wt% PEI with MW = 2,000 g/mol

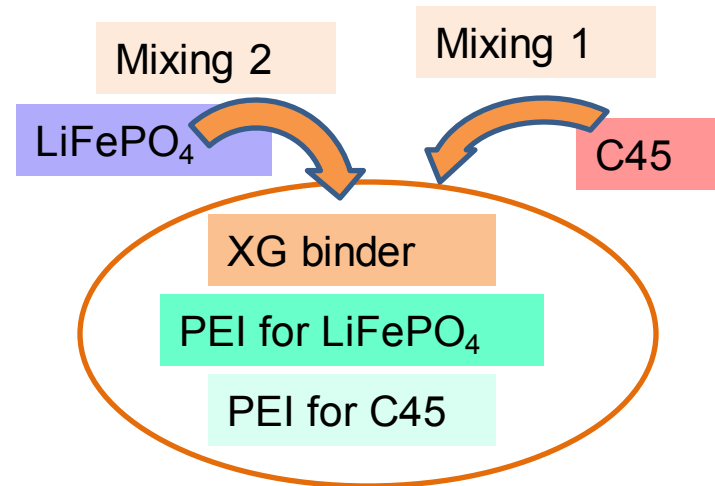
Order of Constituent Addition Is Critical For Aqueous Processing Effectiveness

$\text{LiFePO}_4/\text{C45}/\text{Xanthan Gum}(\text{XG})/\text{PEI}/\text{H}_2\text{O} = 100 / 10 / 2.5 / 2 / 350$ wt fraction

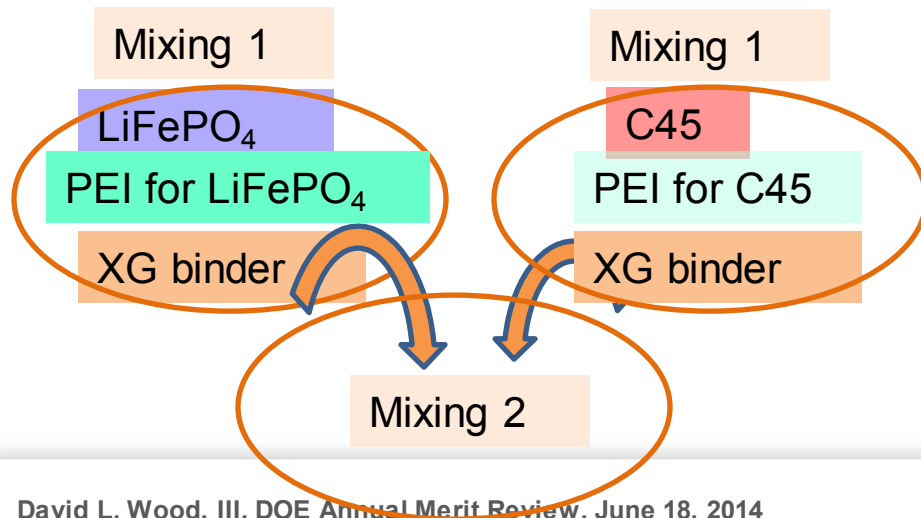
Sequence 1 (S1)



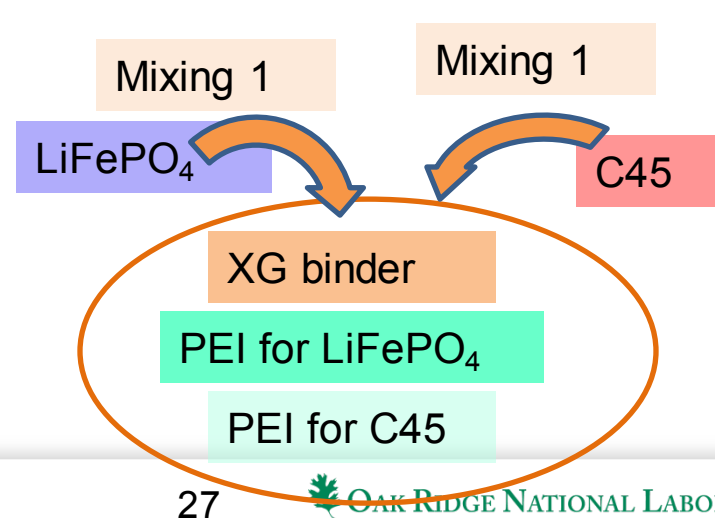
Sequence 2 (S2)



Sequence 3 (S3)

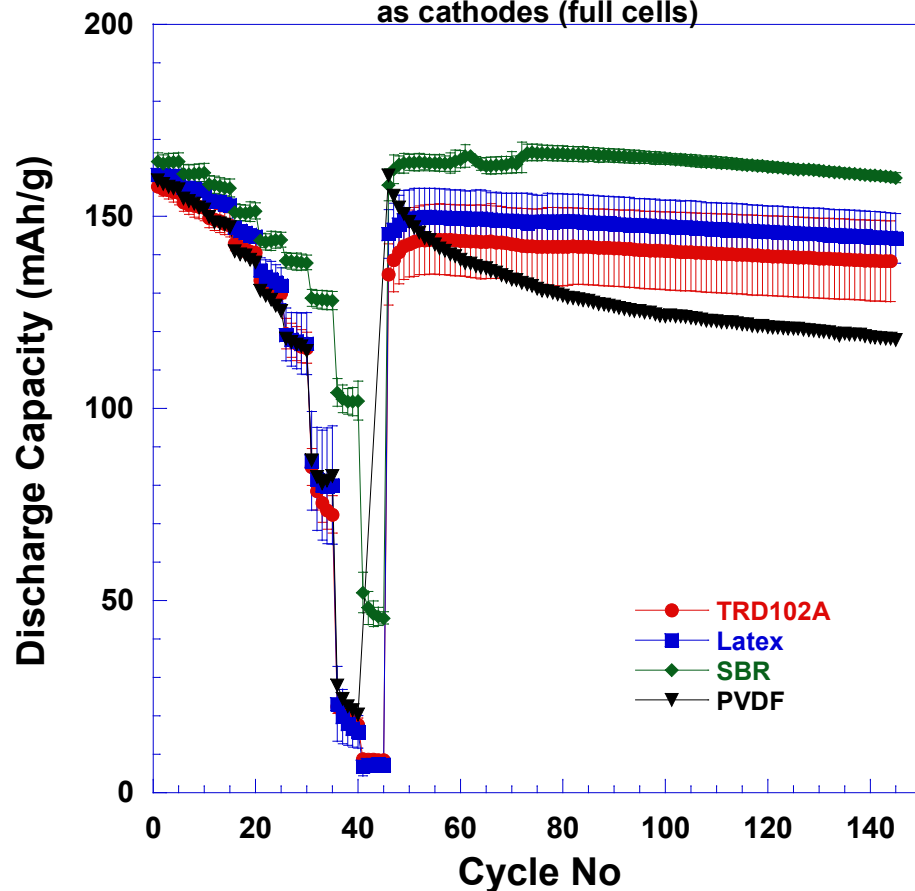


Sequence 4 (S4)



Technical Accomplishments – Successful ConocoPhillips (CP) A12 Graphite Aqueous Processing – Full Cells with NMC 532/NMP

CP A12 with various binders and NMC532/PVDF as cathodes (full cells)



Rate performance comparison of CP A12 anodes with various binders and NMC532/PVDF cathodes (Full cells)

